

THE CALCULATION OF THE THERMODYNAMICAL PROPERTIES IN UNDER- AND OVER-CRITICAL REGION

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Abstract

The paper features the mathematical model of thermodynamic functions of state in over- and under- critical region in the liquid and gas domain for pure refrigerants and mixtures with the help of classical thermodynamics and statistical thermodynamics. To calculate the thermodynamic properties of real fluid the Johnson-Zollweg-Gubbins model based on the modified Benedict-Webb-Rubin equation of state, Chunxi-Yigui-Jiufang equation of state based on simple perturbation theory and complex Tang-Tong-Lu model based on solution the Ornstein-Zernike equation with help of perturbation theory, was applied. To calculate the thermodynamic properties of real fluid with help of classical thermodynamics we used Van Der Waals, Peng-Robinson, Benedict-Webb-Rubin, Benedict-Webb-Rubin-Starling-Nishiumi and Jacobsen-Stewart equation of state. We developed the mathematical model for the calculation of all equilibrium thermodynamical functions of state for pure refrigerants and their mixtures. The analytical results obtained by classical and statistical thermodynamics are compared with the experimental data and show relatively good agreement. This paper presents the first comparison between all presented models obtained by classical and statistical thermodynamics.

Introduction-computation of thermodynamic properties of the state

To calculate thermodynamic functions of state we applied the canonical partition [1]. Utilising the semi-classical formulation for the purpose of the canonical ensemble for the N indistinguishable molecules the partition function Z can be expressed as follows:

$$Z = \frac{1}{N! h^{Nf}} \int \dots \int \exp\left(-\frac{H}{kT}\right) \cdot d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N d\vec{p}_1 d\vec{p}_2 \dots d\vec{p}_N, \quad (1)$$

where f stands for the number of degrees of freedom of individual molecule, H designates the Hamiltonian molecule system, vectors $\vec{r}_1, \vec{r}_2 \dots \vec{r}_N$ describe the positions of N molecules and $\vec{p}_1, \vec{p}_2 \dots \vec{p}_N$ momenta, k is Boltzmann's constant and h is Planck constant. The canonical ensemble of partition function for the system of N molecules can be expressed like this:

$$Z = Z_0 Z_{\text{trans}} Z_{\text{vib}} Z_{\text{rot}} Z_{\text{ir}} Z_{\text{el}} Z_{\text{nuc}} Z_{\text{conf}}. \quad (2)$$

Thus the partition function Z is a product of terms of the ground state (0), the translation (trans), the vibration (vib), the rotation (rot), the internal rotation (ir), the influence of electrons excitation (el), the influence of nuclei excitation (nuc) and the influence of the intermolecular potential energy (conf).

Utilising the canonical theory for computing the thermodynamic functions of the state can be put as follows [2,3]:

$$\begin{aligned} \text{Pressure } p &= kT \left(\frac{\partial \ln Z}{\partial T} \right)_V, \quad \text{Internal energy } U = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V, \\ \text{Freeenergy } A &= -kT \cdot \ln Z, \quad \text{Entropy } S = k \left[\ln Z + T \left(\frac{\partial \ln Z}{\partial T} \right)_V \right], \\ \text{Free enthalpy } G &= -kT \left[\ln Z - V \left(\frac{\partial \ln Z}{\partial T} \right)_V \right], \quad \text{Enthalpy } H = kT \left[T \left(\frac{\partial \ln Z}{\partial T} \right)_V + V \left(\frac{\partial \ln Z}{\partial V} \right)_T \right], \end{aligned} \quad (3)$$

where T is temperature and V is volume of molecular system.

The computation of the individual terms of the partition function and their derivatives except of the configurational integral is dealt with in the works of Lucas [1], McClelland [4] and Münster [5].

The various derivatives and expressions of the fundamental equations (3) have an important physical significance. In These paper are presented expressions which are very important for planning the refrigeration processes. The various derivatives also prove to be of physical interest:

The coefficient of thermal expansion:
$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p. \quad (3)$$

The isothermal compressibility:
$$\chi = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T. \quad (4)$$

The heat capacity at constant volume per mole:
$$C_v = \left(\frac{\partial U}{\partial T} \right)_v. \quad (5)$$

The heat capacity at constant pressure per mole:
$$C_p = \left(\frac{\partial H}{\partial T} \right)_p = C_v + \frac{TV\beta^2}{\chi}. \quad (6)$$

The velocity of sound:
$$c_0 = \sqrt{-V^2 \frac{1}{M} \left(\frac{\partial p}{\partial V} \right)_s} = \sqrt{-V^2 \frac{\frac{C_p}{T} \left(\frac{\partial T}{\partial V} \right)_p \frac{1}{M}}{\left(\frac{\partial V}{\partial T} \right)_p - \frac{C_p}{T} \left(\frac{\partial T}{\partial p} \right)_v}}. \quad (7)$$

The Joule-Thomson coefficient:
$$\mu_J = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right]. \quad (8)$$

Configurational integral

a) Johnson-Zollweg-Gubbins (JZG) model [6]

For a real fluid the Johnson-Zollweg-Gubbins (JZG) model based on molecular dynamics and Monte Carlo simulations with the Lennard-Jones intermolecular potential

is possible to use. The modified BWR equation of state (EOS) contains 32 linear parameters (x_i) and one non-linear parameter (γ) [6].

On this basis we can express configurational free energy A_{conf} :

$$A_{\text{conf}}^* = \sum_{i=1}^8 \frac{a_i \rho^{*i}}{i} + \sum_{i=1}^6 b_i G_i, \quad (9)$$

where the coefficients a_i , b_i and G_i are presented literature [6]. The coefficients a_i and b_i are functions of reduced temperature T^* only, the coefficients G_i are function of the reduced density ρ^* and nonlinear adjustable parameter γ .

$$\rho^* = \frac{N\sigma^3}{V}, \quad T^* = \frac{kT}{\varepsilon}, \quad A_{\text{conf}}^* = \frac{A_{\text{conf}}}{N\varepsilon}, \quad F = \exp(-\gamma \rho^{*2}), \quad \gamma=3, \quad (10)$$

where A_{conf} is reduced configurational free energy, σ and ε are Lennard-Jones parameters.

Equation (9) accurately correlates the thermophysical properties from the triple point to about 4 to 5 times the critical temperature. In equation (9) are x_i 's the adjustable parameters in the equation of state.

With help of configurational free energy we can calculate all configurational thermodynamic properties. Expressions for calculation of configurational entropy and internal energy are shown in literature [6]. We carried out all other expressions for calculation of thermophysical properties.

b) Revisited Cotterman model (CYJ) [7,8]

Revisited Cotterman EOS is based on the hard sphere perturbation theory. The average relative deviation for pressure and internal energy in comparison with Monte-

Carlo simulations are 2.17% and 2.62% respectively for 368 data points [8]. The configurational free energy is given by:

$$A_{\text{conf}} = A^{\text{hs}} + A^{\text{pert}}, \quad (10)$$

$$\frac{A^{\text{hs}}}{R_m T} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2}, \quad A^{\text{pert}} = \frac{A^{(1)}}{T^*} + \frac{A^{(2)}}{T^*}, \quad (11)$$

$$\frac{A^{(1)}}{R_m T} = \sum_{m=1}^4 A_{1m} \left(\frac{\eta}{\tau} \right)^m, \quad \frac{A^{(2)}}{R_m T} = \sum_{m=1}^4 A_{2m} \left(\frac{\eta}{\tau} \right)^m, \quad (12)$$

$$\tau = 0.7405, \quad \eta = \frac{\pi \rho D^3}{6}.$$

where η is packing factor, D is hard-sphere diameter. With help of configurational free energy we can calculate all configurational thermodynamic properties. Expressions for calculation of configurational entropy and internal energy are shown in literature [7]. We carried out all other expressions for calculation of thermophysical properties.

c) Tang-Tong-Lu model [9]

Tang-Tong-Lu model uses as the intermolecular potential a new two-Yukawa function. This function is found to mimic very closely the Lennard-Jones potential. Tang-Tong-Lu analytical model calculates thermodynamic functions of state on the base of salvation of the Ornstein-Zernike equation with help of perturbation theory. Comparisons with the computer simulation data indicate that the developed expressions yield better results (pressure, internal energy, free energy) than theory of Weeks et al. [1], Barker and Henderson [5]. Results of pressure, internal energy and free energy obtained by TTL model are comparable with the most recent modified Benedict-Webb-Rubin EOS. The configurational free energy is given by:

$$\frac{A_{\text{conf}}}{NkT} = a_0 + a_1 + a_2, \quad (13)$$

where a_0 represents the free energy of the hard sphere fluid, a_1 and a_2 are perturbed first and second order parts. With help of configurational free energy we can calculate all configurational thermodynamic properties. Expressions for calculation of configurational entropy and internal energy are shown in literature [9]. We carried out all other expressions for calculation of thermophysical properties.

Mixtures

The thermodynamic properties of Lennard-Jones mixtures are obtained using the one fluid theory [10]. The molecules interacting with Lennard-Jones potential have parameters σ and ϵ given by:

$$\sigma^3 = \sum_{\alpha,\beta} \psi_{\alpha} \psi_{\beta} \sigma_{\alpha\beta}^3, \epsilon \sigma^3 = \sum_{\alpha,\beta} \psi_{\alpha} \psi_{\beta} \epsilon_{\alpha\beta} \sigma_{\alpha\beta}^3. \quad (18)$$

$$\sigma_{\alpha\beta} = \frac{\sigma_{\alpha\alpha} + \sigma_{\beta\beta}}{2}, \epsilon_{\alpha\beta} = \sqrt{\epsilon_{\alpha\alpha} \epsilon_{\beta\beta}}. \quad (19)$$

Results And Comparison With Experimental Data

The constants necessary for the computation such as the characteristic rotation-, vibration-, electronic etc. temperatures are obtained from experimental data [11,12,13]. The inertia moments are obtained analytically by applying the knowledge of the atomic structure of the molecule. Constants for Lennard-Jones potential are obtained from the literature [14].

Table 1 shows used models obtained by classical thermodynamics (Van der Waals EOS (VDW) [22], Peng-Robinson (PR) [22], Redlich-Kwong (RK) [22], Benedict-

Webb-Rubin [22] (BWR), Benedict-Webb-Rubin-Starling-Nishiumi [23,24] (BWRSN) and Jacobsen-Stewart [25] (JS), the number of constants and their influence on polarity. The further calculation of thermodynamical functions of state on the base of fugacity coefficient and chemical potential with help of classical thermodynamics is well-known matter and is not described in this paper [26].

We carried out calculations for ammonia R 717(NH₃) carbon dioxide R 744 (CO₂), methane R 50 (CH₄) and Argon R 740 (Ar) . The comparison of our calculations with experimental results and thermodynamical data (Exp.) [15-22] are presented in Tables 2-10.

Tables 2, 3 and 4 represent the deviation of the results in the real gas region between the analytical computation and experimental data.

Table 2 shows the results for ammonia for the real gas region between the analytical computation obtained by statistical thermodynamics (ST- statistical theory with help of classical virial expansion [5], JZG Johnson-Zollweg-Gubbins model, TTL-Tang-Tong-Lu model and CYJ Chunxi-Yigui-Jiufang model), models obtained by classical thermodynamics (Table 1) and the experimental values (Exp). At the procedure of computing the configurational integral with the help of statistical thermodynamics on the base of classical virial expansion (ST) the effects of mutual interactions up to three molecules in the cluster were taken into account. The computed pressure conform well for all models, obtained by statistical thermodynamics, with the measured values. Larger deviations can be found in the region of critical conditions due to the large influence of non-isotropic multipolar interactions. The results for all models obtained by statistical thermodynamics show relatively good agreement. Table 3 shows the results for carbon dioxide in the region of saturated vapour. The computed velocity of sound conform well

for all models, obtained by statistical thermodynamics, with the measured velocity of sound. Somewhat larger deviations can be found in the region of critical conditions due to the large influence of fluctuation theory [27] and singular behaviour of some thermodynamic properties in the near-critical condition. Table 4 shows the deviation of the results for air for Joule-Thomson coefficient between the analytical computation and experimental results. The results of the Joule-Thomson coefficient agree considerably well with the measured values. The perturbation models TTL and CYJ yield surprisingly good results.

Tables 5 and 6 represent the deviation of the results in the real liquid region between the analytical computation and experimental data for argon and carbon dioxide. Somewhat larger deviations can however be found in the region of real liquid due to the large influence of the attraction forces, since the Lennard-Jones potential is only an approximation of the actual real intermolecular potential. The best results in the real liquid domain are obtained with the classical JS model. The comparison between computed analytical results obtained by the statistical thermodynamics and measured one shows slightly less good agreement of results. A considerable deviation of results from the measured values is observed in case of carbon dioxide (Table 6) which is ascribed to the influence of the multipole, induced and dispersion intermolecular non-isotropic forces.

Tables 7 and 8 represent the deviation of the results in the real liquid region between the analytical computation and experimental data for mixtures of refrigerants. JS model is not appropriate for the calculation of thermodynamic functions of state of mixtures

Conclusion And Summary

The paper presents the mathematical model for computation of thermodynamical functions of the state in the real liquid and gaseous region. For the real fluid the Johnson-Zollweg-Gubbins model based on molecular dynamic and Monte Carlo simulations and modified Benedict-Webb-Rubin equation of state. Tang-Tong-Lu complex perturbation model and Chunxi-Yigui-Jiufang model was applied. We developed the expressions for the calculation the velocity of sound, thermal expansion coefficient....

The analytical results are compared with the experimental results and analytical calculation obtained by classical thermodynamics and show relatively good agreement. In comparison with experimental data, somewhat larger deviations can however be found for polar fluids in the region of higher densities due to the large influence of the attraction forces, since the Lennard-Jones potential is only an approximation of the actual real intermolecular potential.

Nomenclature

A	free energy
A^*	reduced free energy
BWR	Benedict-Webb-Rubin
BWRSN	Benedict-Webb-Rubin-Starling-Nishiumi
c_0	velocity of sound
C_p	heat capacity at constant pressure per mole
C_v	heat capacity at constant volume
CYJ	Chunxi-Yigui-Jiufang model
D	hard sphere diameter

E	potential energy
Exp	experiment
f	number of degrees of freedom
G	free enthalpy
H	enthalpy, hamiltonian
h, \hbar	Planck constant
JS	Jacobsen-Stewart
JZG	Johnson-Zollweg-Gubbins
k	Boltzmann constant
M	molecular mass
N	number of molecules in system
p	pressure, momentum
PR	Peng-Robinson
R_m	universal gas constant
RK	Redlich-Kwong
S	entropy
ST	statistical virial theory
T	temperature
T^*	reduced temperature
TTL	Tang-Tong-Lu model
U	internal energy
V	volume
VDW	Van der Waals
Z	partition function

β	coefficient of thermal expansion
ε	Lennard-Jones parameter
η	packing factor
μ	chemical potential
ρ	density
ρ^*	reduced density
μ_J	Joule-Thomson coefficient
ψ_i	mole fraction of component i
χ	isothermal compressibility
σ	Lennard-Jones parameter

References

- [1] K. Lucas, Applied Statistical Thermodynamics, Springer - Verlag, New York, 1992.
- [2] T. Kihara, Intermolecular Forces, University of Tokyo, John Wiley & Sons, Cichester, New York, Brisbane, Toronto, 1976.
- [3] N.A. Smirnova, Methods of the Statistical thermodynamics in the Physical Chemistry, University of Moscow, Moscow, 1982.
- [4] B.J. McClelland, Statistical Thermodynamics, Chapman & Hall, London, 1980.
- [5] A. Münster, Statistical Thermodynamics, Springer - Verlag, New York, 1974.
- [6] J.K. Johnson, J.A. Zollweg, K.E. Gubbins, Mol. Phys., 78 (1993) 591-618.
- [7] L. Chunxi, L. Yigui, L. Jiufang, Fluid Phase Equilibria, 127 (1997) 71-81.
- [8] R.L. Cotterman, B.J. Shwarz, J.M. Prausnitz, AIChE Journal, 32 (1986) 1787-1798.
- [9] Y. Tang, Z. Tong, B.C.-Y. Lu, Fluid Phase Equilibria 134 (1997) 20-42.

- [10] B.J. Moser, Die Theorie der Intermolekularen Wechselwirkungen und ihre Anwendung auf die Berechnung von Verdampfungsgleichgewichten binärer Systeme, Ph. Thesis, 1981.
- [11] L.J. Bellamy, The Infrared Spectra of Complex Molecules", Chapman & Hall, London, 1980.
- [12] G. Herzberg G., Electronic Spectra of Polyatomic Molecules, Van Nostrand Reinhold Company, London. Toronto, Melbourne, 1966.
- [13] G. Herzberg, Infrared and Raman Spectra of Polyatomic molecules, Van Nostrand Reinhold Company, New York, 1984.
- [14] O.O. Hirschfelder, C.F. Curtiss, R.B. Bird, Molecular Theory of Gases and Liquids, John Wiley & Sons, London, 1954.
- [15] J.B. Maxwell, Data Book on Hydrocarbons, Van Nostrand Company, New York, 1955.
- [16] W.C. Edmister, B.I. Lee B.I., Hydrocarbon Thermodynamics I,II, Gulf Publishing Company, London, 1964.
- [17] R.L. Eckert, R.M. Drake, Heat and Mass Transfer, McGraw-Hill Company, New York, 1959.
- [18] J. Petrak, L. Ludek, Termokinetic Properties of Refrigerants, Faculty of Mechanical Engineering, Prague, 1993.
- [19] B.A. Younglove, N.V. Frederick, R.D. McCarthy, Speed of Sound Data and Related Models for Mixtures of Natural Gas Constituents, NIST, Washington, 1993.
- [20] C. Borgnakke, R.E. Sonntag, Thermodynamic and transport properties, John Wiley & Sons, New York, 1997.

- [21] E. Ermakova, J. Solca J., Huber H. Marc Welker, Argon in condensed phase, The Journal of Chemical Physics, 102 (1995) 4943-4951.
- [22] K. Wark, Advanced Thermodynamics for Engineers, McGraw-Hill, 1995.
- [23] H. Nishiumi, S. Saito, Journal of Chem. Engin. Jap., 8 (1975) 356-361.
- [24] H. Nishiumi, Journal of Chem. Engin. Jap., Vol. 13 (1980) 178-183.
- [25] Jacobsen, R.T., Stewart, R.B., Jahangiri, M., S.G. Penoncello, Advances in Cryogenic Engineering, 31 (1986) 1161-1169.
- [26] S.M. Walas, Phase Equilibria in Chemical Engineering, Bittenworth Publishers, Boston, 1984.
- [27] A. Pelt, J.V. Sengers, The Journal of Supercritical Fluids, 8 (1995) 81-99.

TABLES

Table1. Fundamental characteristics of various EOS obtained on the base of classical thermodynamics.

EOS	Number of used constants	Influence of polarity	Region
VDW	2	NO	Real gas, mixtures
RK	2	NO	Real gas
PR	3	YES	Real gas,Phase transition
BWR	8	NO	Real gas
BWRSN	16	YES	Real gas, real liquid
JS	40-150	YES	Real gas, Real liquid

Table 2. Saturation pressure for ammonia (R 717)

T [K]	263	283	303	323	343	363	383
	p (bar)						
VDW	3.53	6.44	12.6	21.9	35.4	57.2	83.7
PR	3.42	6.29	12.2	21.7	34.3	52.5	76.9
RK	2.99	6.29	12.3	21.7	35.3	53.4	79.7
BWR	2.99	6.22	11.6	20.7	34.3	52.2	76.8
BWRSN	2.97	6.29	12.2	21.6	35.3	55.2	81.4
JS	2.89	6.21	11.6	20.3	33.0	50.9	74.7
ST	2.96	6.20	12.7	22.9	38.8	63.7	106
JZG	3.03	6.21	12.7	22.8	38.7	63.3	104
CYJ	3.02	6.22	12.7	22.9	38.8	63.7	106
TTL	3.02	6.22	12.8	23.0	38.9	64.0	107
Exp.	2.91	6.16	11.6	20.3	33.1	51.0	75.6

Table 3. The speed of sound c_0 for carbon dioxide (R 744) (saturated vapour)

T [K]	263	273	283	293	301
	c_0 [m/s]				
VDW	216.1	209.0	202.4	188.0	180.2
PR	218.4	217.0	214.7	204.8	139.1
RK	220.1	214.2	205.5	181.9	92.9
BWR	214.9	210.6	204.4	195.8	188.2
BWRSN	214.6	210.5	205.3	199.8	198.7
JS	216.7	211.5	204.5	195.4	184.4
ST	217.9	223.5	209.9	208.6	219.3
JZG	219.3	219.3	212.9	203.7	194.1
CYJ	223.8	219.9	213.8	204.2	191.0
TTL	226.4	223.2	218.1	210.2	199.1
Exp.	217.5	212.7	206.3	197.9	189.8

Table 4. Comparison of the Joule Thomson coefficient calculation for air (R-729)

μ_J [K/bar]:					
T [K]	150	150	400	800	800
p [bar]	1	50	50	1	50
VDW	.623	.674	.145	.007	.007
PR	.858	.630	.124	-.033	-.036
RK	.782	.581	.105	-.019	-.024
BWR	.766	.560	.103	-.028	-.034
BWRSN	.793	.596	.086	-.014	-.0284
JS	.813	.643	.090	-.029	-.032
ST	.750	.711	.110	-.017	-.023
JZG	.799	.711	.109	-.022	-.022
CYJ	.829	.788	.109	-.028	-.031
TTL	.750	.695	.110	-.024	-.028
Exp.	.804	.644	.091	-.030	-.034

Table 5. The isothermal compressibility for argon (R 740) in the region of compressed liquid

T [K]	110	200	300	400	500
V [m³/kmol]	.0317	.0329	.1187	.0507	.0602
χ [Gpa⁻¹]					
BWRSN		1.87	43.5	43.5	4.15
JS	4.09	2.27	47.6	5.1	6.05
JZG	4.09	2.39	40.40	4.9	5.9
CYJ		2.50	40.80	5.23	6.04
TTL	4.09	2.38	38.71	5.04	5.80
Exp.	3.42		42.96		

Table 6. The coefficient of thermal expansion for carbon dioxide in the region of boiling

liquid					
T [K]	253	263	273	283	293
V [m ³ /kmol]	.0427	0.044	.0475	.051	.0568
β [1/K]					
BWRSN	.0042	.0052	.0081	.0137	.028
JS	.0044	.0053	.0073	.0106	.035
JZG	.0043	.0054	.0075	.0110	.0261
CYJ	.0041	.0050	.0065	.0062	.0201
TTL	.0028	.0034	.0044	.0093	.0120
Exp.			.0080		.0140

Table 7. The velocity of sound for mixture of 85%R50 in 15%R744

PRESSURE					
c_0 (m/s)					
T	Model	10 bar	40 bar	60 bar	80 bar
250 K	CYJ	363.1	348.0	339.0	334.1
	JZG	362.9	371.1	337.8	333.1
	TTL	363.1	347.6	337.9	331.4
	ST	359.4	346.1	335.6	328.8
	VDW	358.1	331.0	314.8	308.6
	RK	369.8	381.2	412.0	434.1
	BWR	367.5	370.0	371.1	374.1
	BWRSN	365.4	355.6	342.1	341.9
	Exp.	359	342	332	330

Table 8. Calculation of velocity of sound for 85%R50 and 15%R170 mixture at T=350 K

	Pressure			
	5 bar	20 bar	60 bar	80 bar
CYJ	448.3	446.5	443.9	443.9
JZG	448.2	446.0	443.0	443.1
TTL	448.2	446.1	442.8	442.6
ST	448.1	446.7	441.1	441.5
VDW	446.1	440.0	428.7	426.5
RK	446.7	442.7	436.9	436.1
BWR	446.9	443.5	438.7	438.7
BWRSN	448.1	443.2	441.1	443.1
Exp.	448	444.7	441	442